Development of Modeling and Scaling Methods for Predicting Coupled Reactive Transport Processes

Auburn University
University of Alabama
Brigham Young University
and
University of Wisconsin
Pacific Northwest National Laboratory
(collaborators)

The research team

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  - Prof. Prabhakar Clement, (PI/PD)
  - Prof. Mark Barnett (co-PI)
- Department of Geological Sciences, University of Alabama, Tuscaloosa
  - Prof. Chunmiao Zheng (co-PI)
- Department of Civil and Environmental Engineering, Brigham Young University
  - Prof. Norman Jones (co-PI)
- Collaborators
  - Prof. Eric Roden (UW), Chris Johnson and Mike Truex (PNNL)

Motivation

<u>ERSP mission:</u> Provide sufficient scientific understanding for incorporating coupled physical, chemical and biological processes into decision making for environmental remediation..

<u>Needs:</u> Develop methods for scaling geochemical reactions (from molecular, mineral surface and pore levels to larger scales) to understand the fate and transport of DOE contaminants in the subsurface…

Our goal is to address these ERSP mission/needs..

We will focus on coupled physical and chemical processes

If you are wondering about the genomes of our organism, I am sorry to disappoint you… no "ABCDEFGHIJK" data in this talk! Instead, we will learn some Greek $"\alpha, \beta, \sum, \frac{\partial^2 c}{\partial y^2}"$

Warning: If you are the disappointed microbiologist thinking of taking an early coffee break.. think again! Mike, Paul, Todd and David are watching!

Project Objectives

- Develop methods for scaling uranium (cation) and arsenic (an analog for oxy anions) sorption reactions with sediments containing iron oxides
- Develop methods for scaling arsenic sorption and oxidation reactions with MnO_2 (pyrolusite) minerals
- Demonstrate the relevance of scaling models for a remediation technology that uses hydroxyapatite to treat uranium
- Develop 2-D datasets for validating numerical reactive transport models
- Develop methods to build a computationally efficient, scalable, MODFLOW-family reactive transport model (RT3D)

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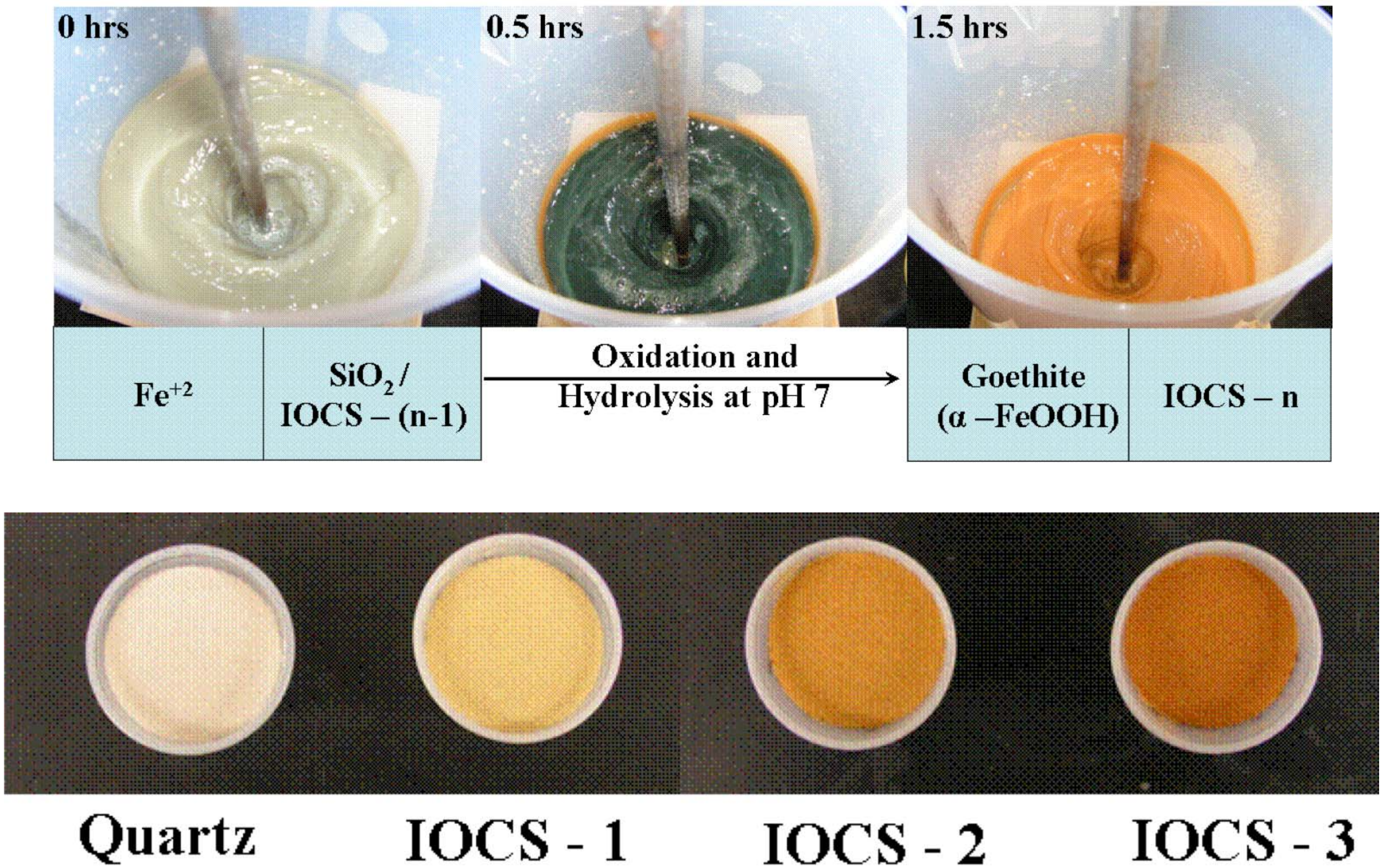
Develop reaction scaling approaches for uranium and arsenic sorption

- Hypothesis: The properties of iron oxides associated with natural sediments (type of coating, amount, and surface area) will control metal sorption.
  - Sorption reaction should be scalable to one of these (or a combination of these) soil parameters

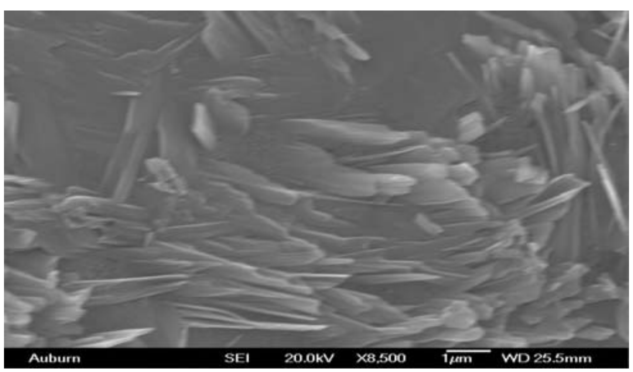
- Experimental approach: Synthesize well-characterized iron-coated sands with varying amounts of iron, and use them to tease out the scaling parameters that control sorption

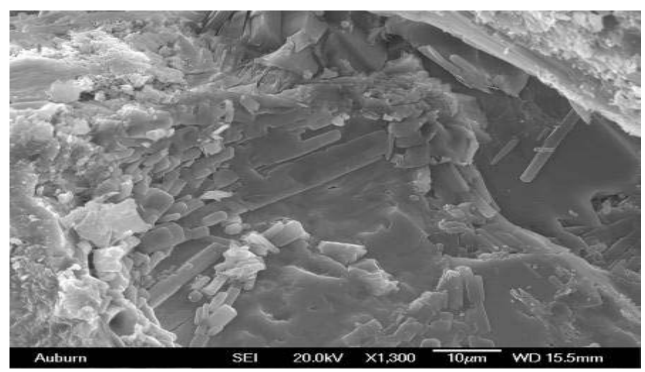
Synthesis of iron coated sand with different Fe content



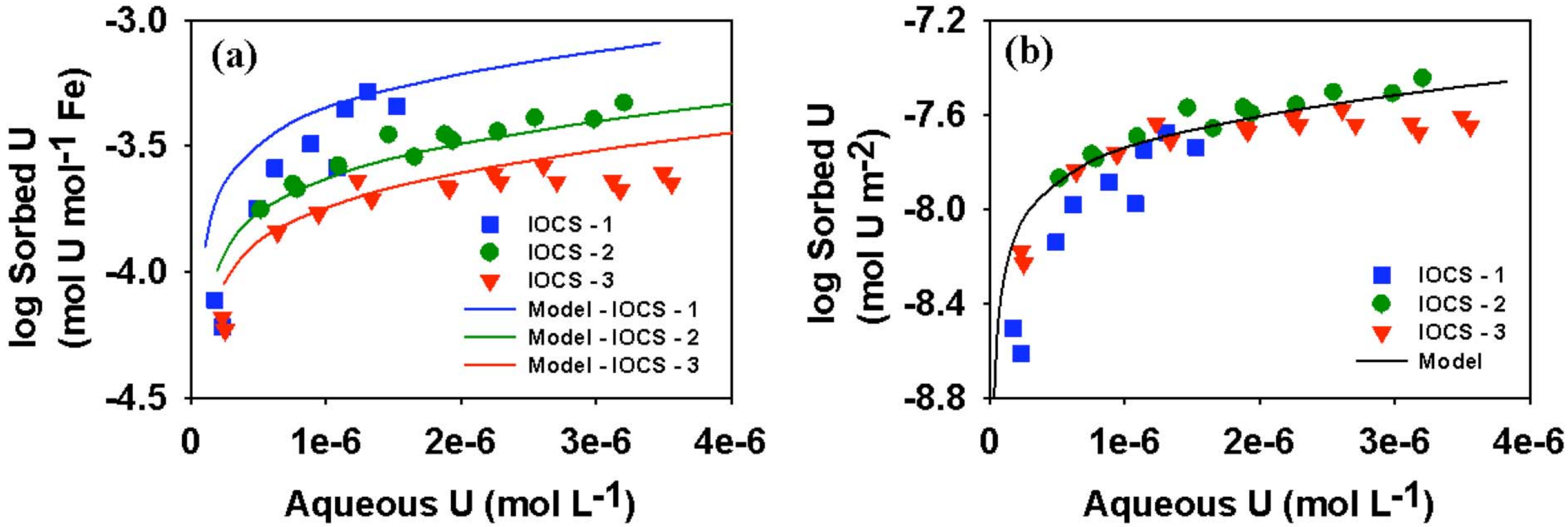
Characterization of the sands

System	Sand	DCB Fe	Surface Area
		(%)	$m^2\ g^{-1}$ of material
Pure quartz		0	0.0348
IOCS – 1		0.040 ± 0.001	0.1771
IOCS – 2		0.182 ± 0.005	0.4279
IOCS – 3		0.315 ± 0.007	0.5652





Uranium sorption data and Waite et al. surface complexation model results



Adsorption of U(VI) to IOCS at pH 4.45 ± 0.1 and ionic strength of 0.1 M. (a) scaled to iron content; (b) scaled to specific surface area. The lines represent the predictions of Waite et al. (1994) model.

Scaling U(VI) sorption data and model results

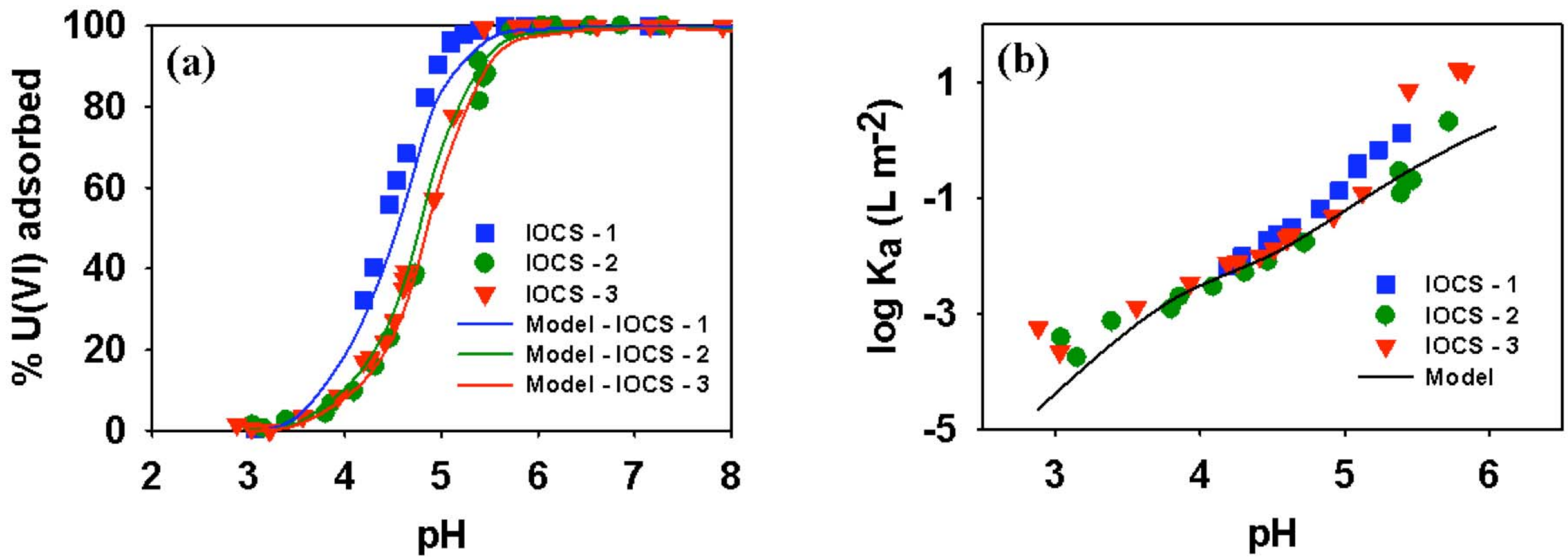


Fig (a) U(VI) adsorption edges onto IOCS at a total initial U(VI) concentration of 4.2 µM and ionic strength of 0.1 M; (b) when scaled to specific surface area. The lines represent the predictions of Waite et al. (1994) model.

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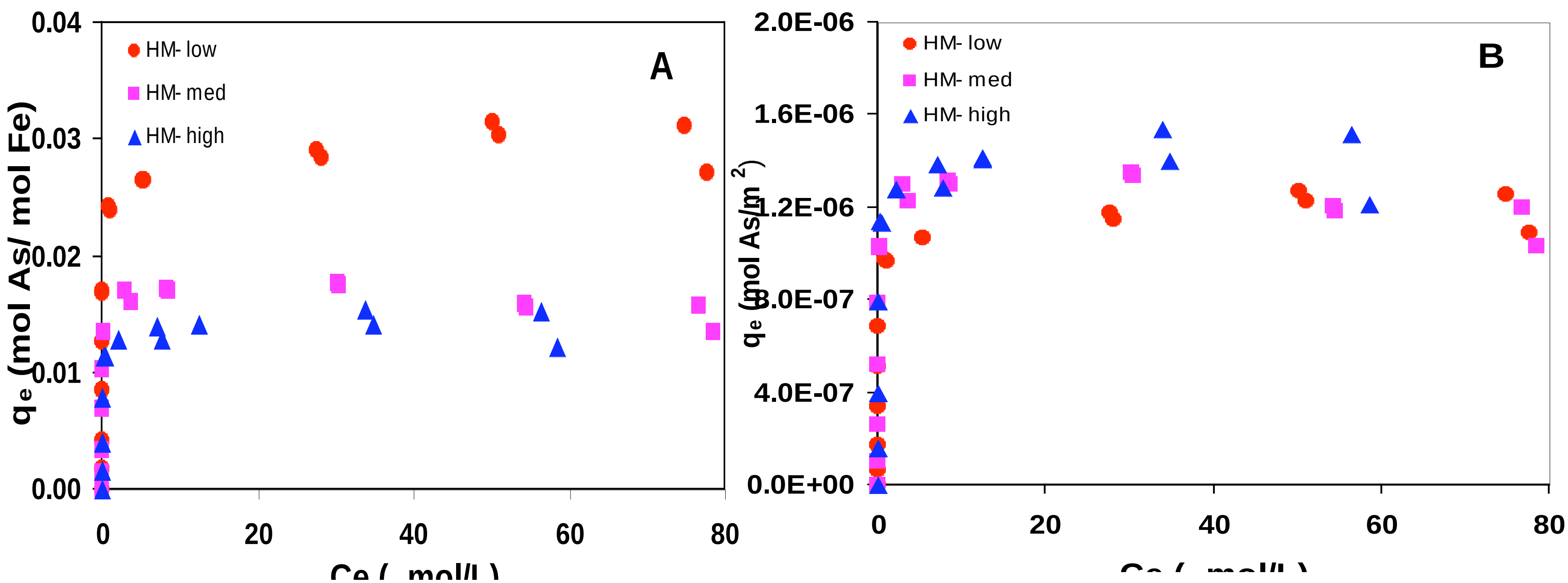
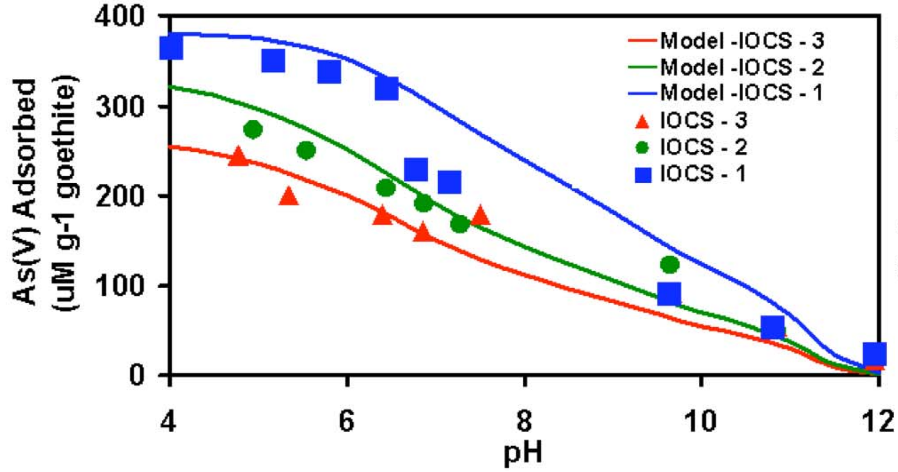
Scaling As(V) sorption on IOCS

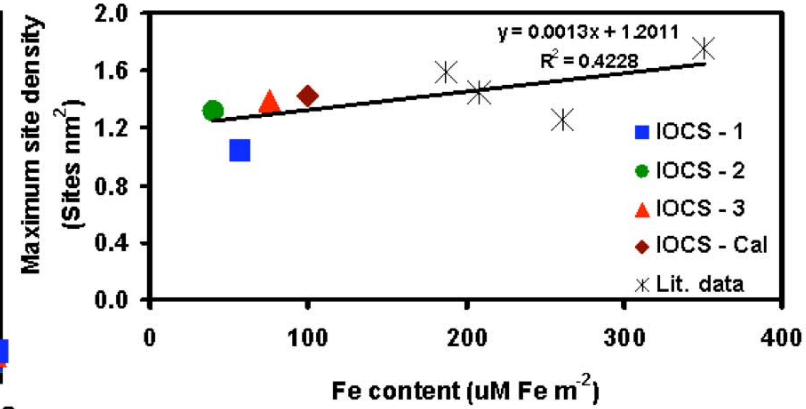


Comparison of adsorption isotherms normalized to A) Fe content and B) surface area for three laboratory- synthesized Fe- coated sands. Experimental conditions: pH= 7±0.2; I=0.01M; T=22°C.

As(V) sorption data and scaled surface complexation model results

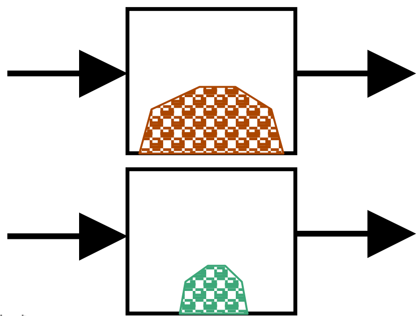


Scaled model and data for Arsenic adsorption onto IOCS

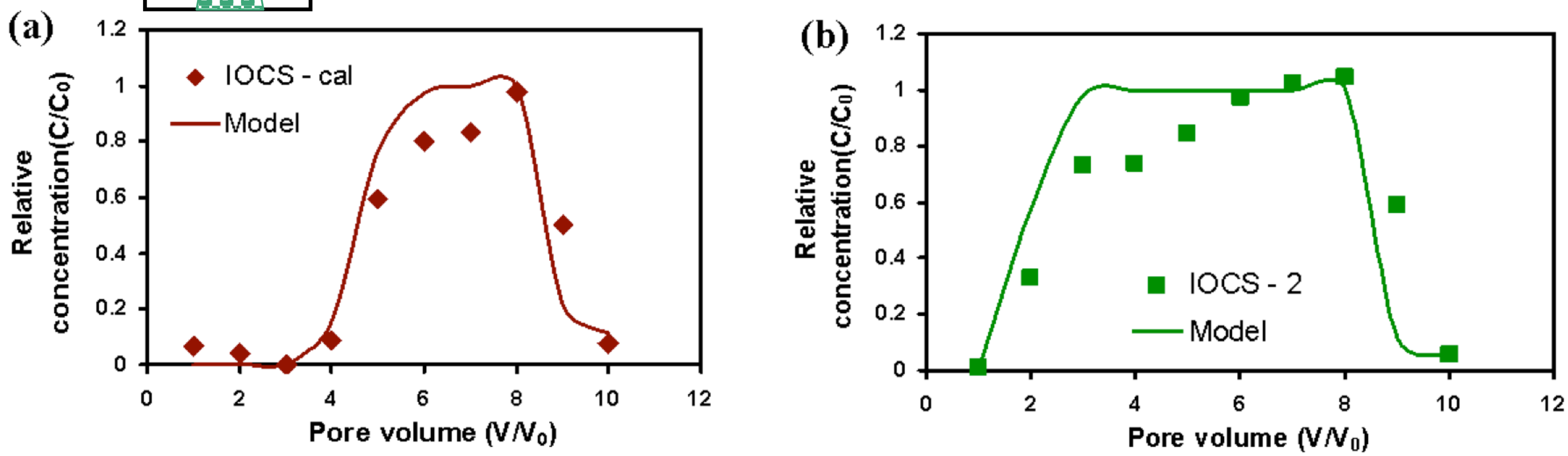


Relationship between maximum adsorption site density and iron content used in the model

Moving from batch to 1-D transport Sequencing batch reactor experiments



Analog for transport through a single node (vary soil types and solid-to-solution ratio)

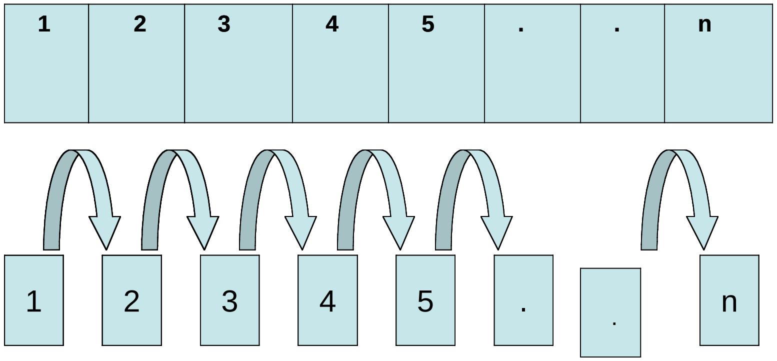


Scaled model applied for predicting breakthrough profiles of As(V) from multi-pore volume batch reactor at pH 4. SSR: 30 g IOCS L^{-1}; C_0: 1 mg L^{-1}. IOCS-cal has 0.35% Fe and surface area of 310 m^2 g^{-1} Fe. IOCS-2 has 0.18% Fe and surface area of 234 m^2 g^{-1} Fe

Planned/on-going experiments

- Conduct sequential batch reactor studies

  Analog for transport through a 1-D column (Advantages: Establishment of equilibrium, also we can vary solid-to-solution ratios)



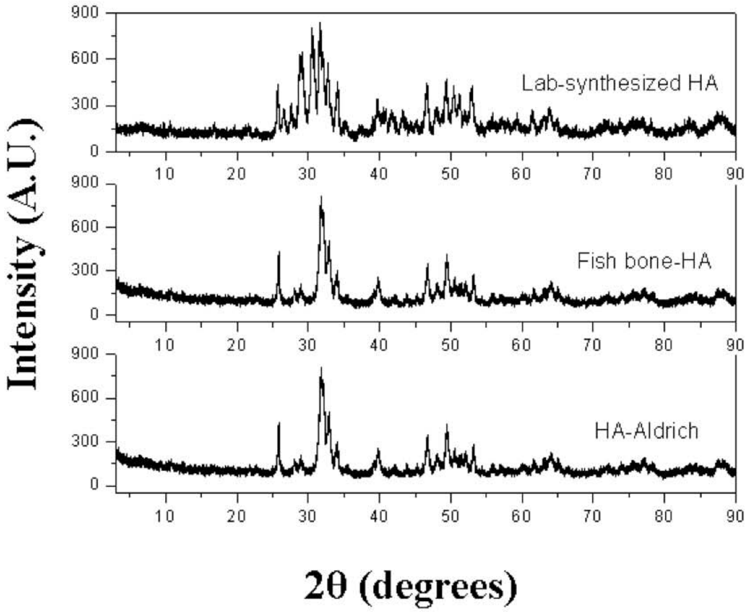
- Column-scale experiments
- Two dimensional soil box experiments

Implication to environmental remediation: Case study – Remediation of uranium using various types of hydroxyapatites

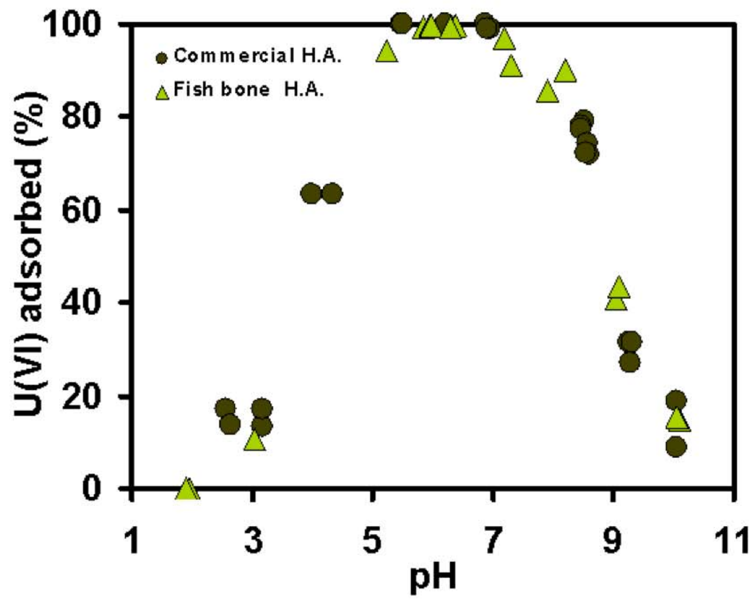
- Hydroxyapatite is an excellent material for removing uranium. Our goal is to develop a fundamental model for describing coupled physical and chemical processes associated with this remediation technology
- We have used three types of HA
  - Commercial HA from Aldrich
  - Lab synthesized nano-HA*
  - Processed HA from Ictalurus punctatus (channel catfish) bones

*Nano hydroxyapatite was synthesized by reacting $Ca(NO_3)_2 \cdot 4H_2O$ (0.1M) and phosphoric acid (H_3PO_4) (0.05M) and adding drop wise concentrated NH_4OH.

Uranium remediation using various hydroxyapatites

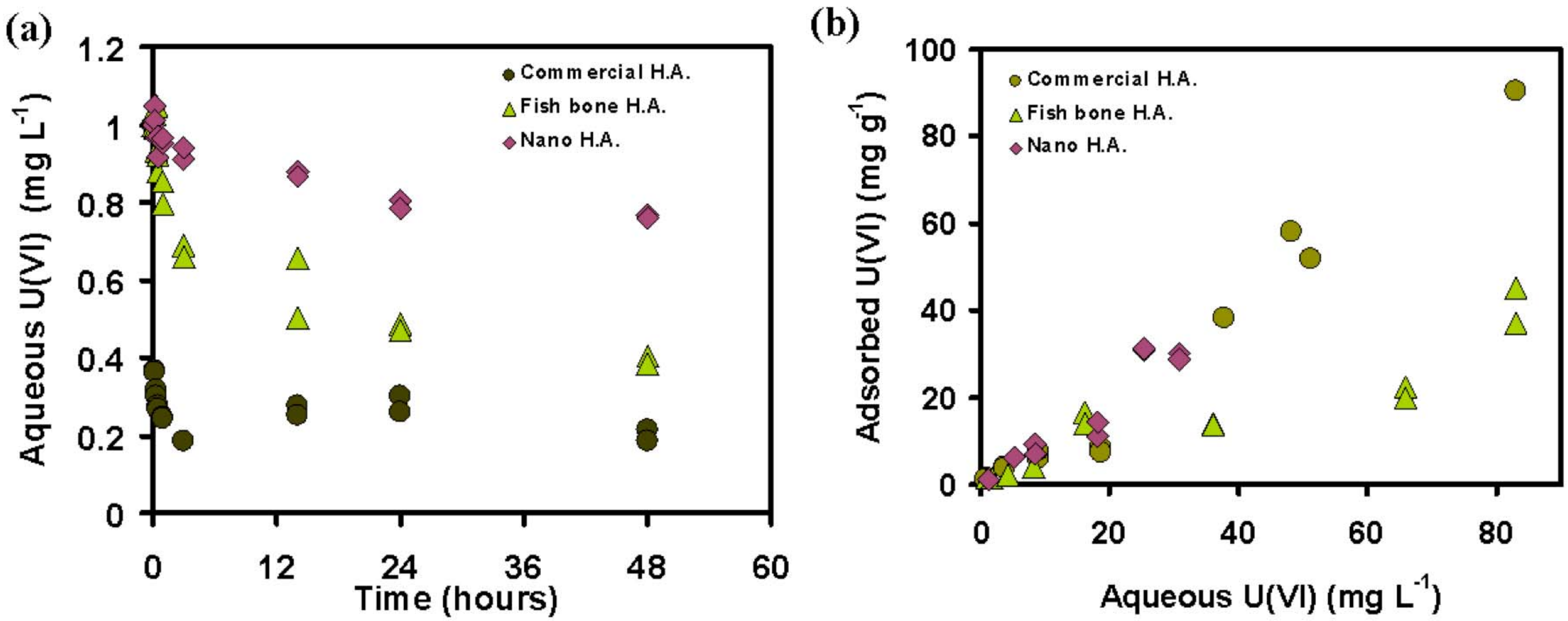


Powder XRD patterns of hydroxyapatite derived from various sources



Adsorption edges of 1 mg L^{-1} U(VI) by 0.5 g L^{-1} of hydroxyapatite

Uranium remediation using various hydroxyapatites



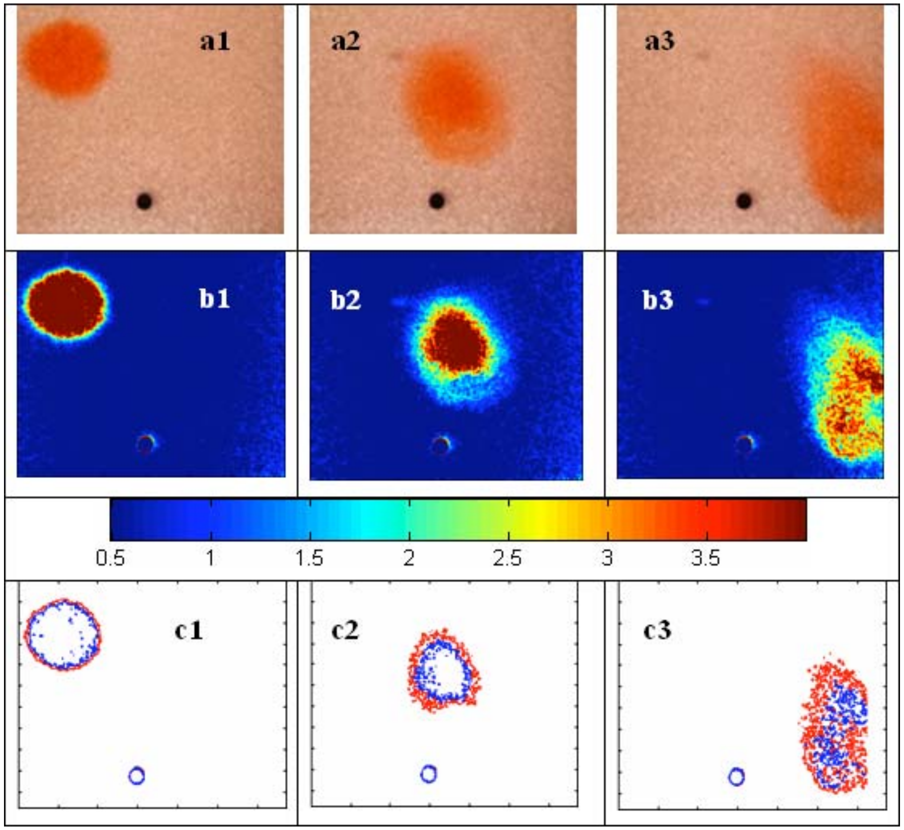
U(VI) adsorption onto different types of hydroxyapatite (0.5 g L^{-1}) at pH 8.5

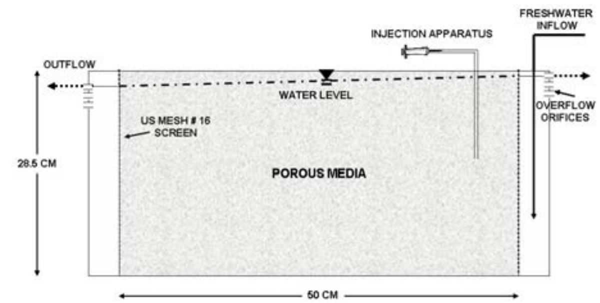
(a) Batch kinetics (b) Batch isotherm

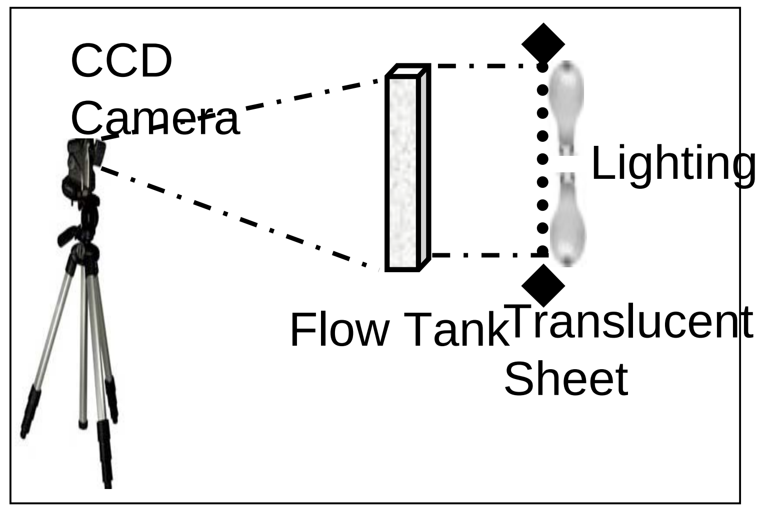
Future work related to hydroxyapatite

- Develop a scalable surface complexation modeling framework for predicting HA interactions with uranium
- Couple the SC model with a transport code and use it to design various types of remediation experiments
- Conduct laboratory scale, two-dimensional reactive transport experiments (barrier or in situ injection technologies) in soil boxes using different types of HA (benchmark datasets)

Two-dimensional soil tank experiments (image analysis)

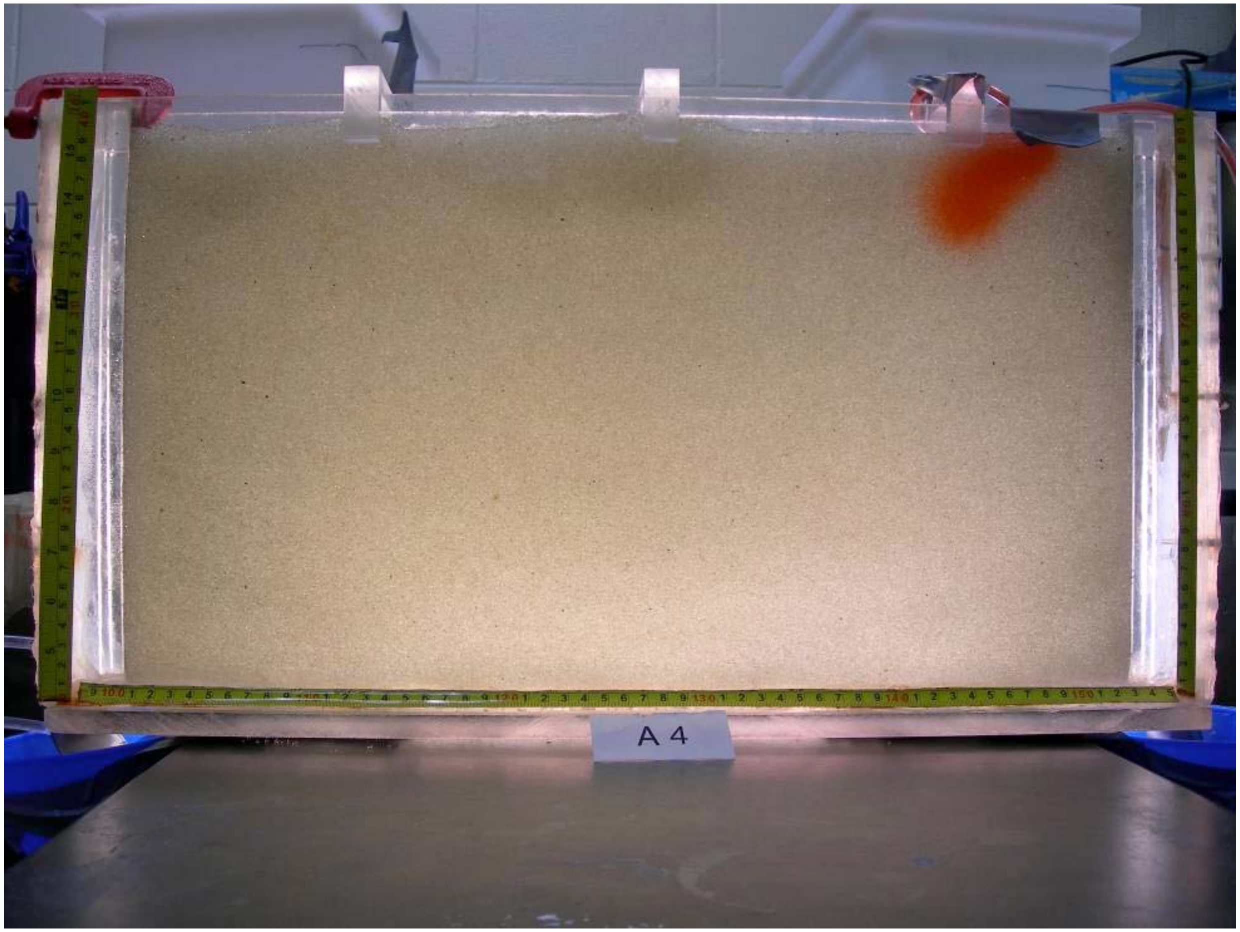


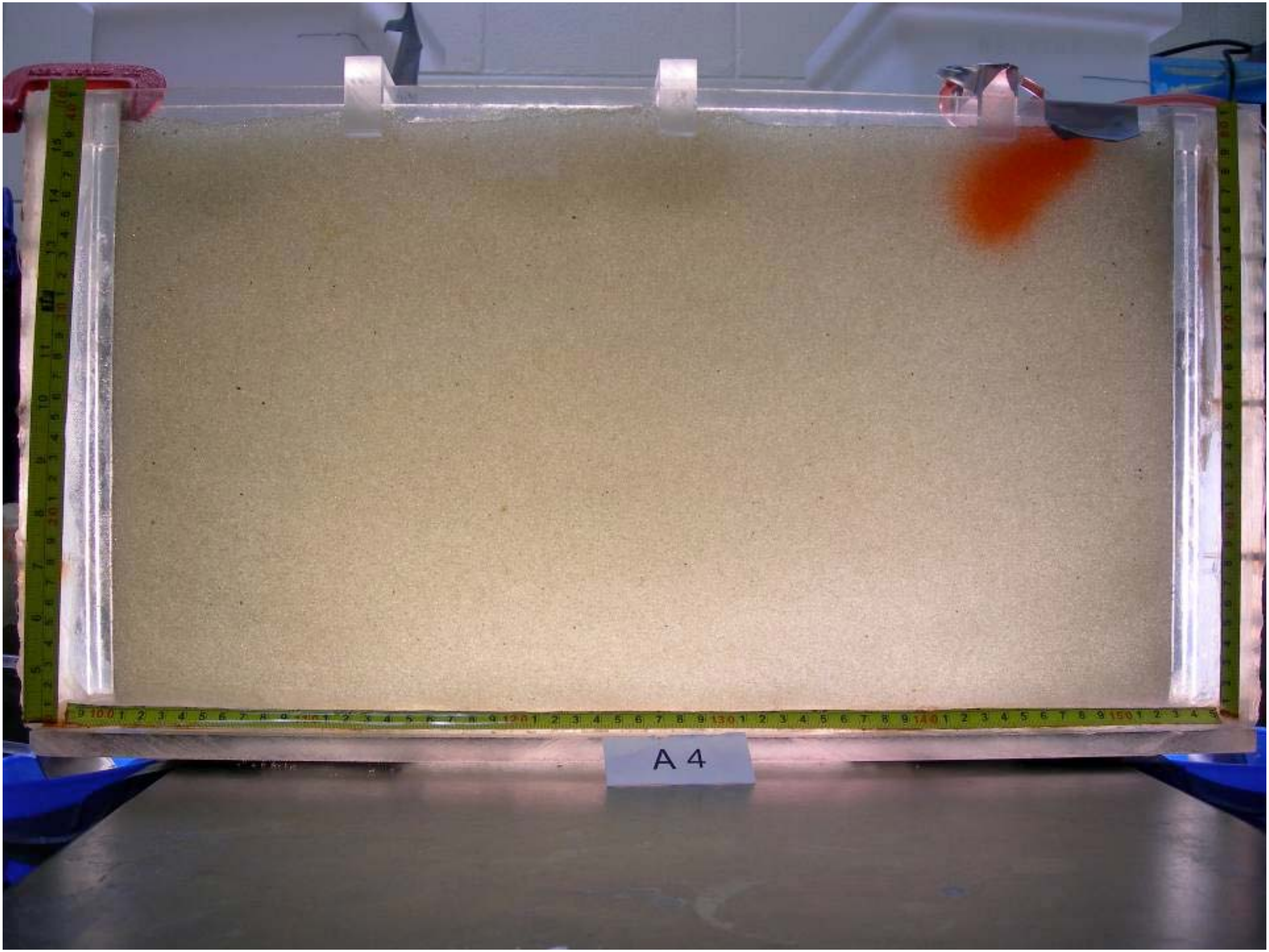




Goswami, R.R., B. Ambale and T. P. Clement, Error Estimation of Concentrations Measurements obtained from Image Analysis in porous media, ***Vadose Zone Journal,*** submitted.

Transport experiments

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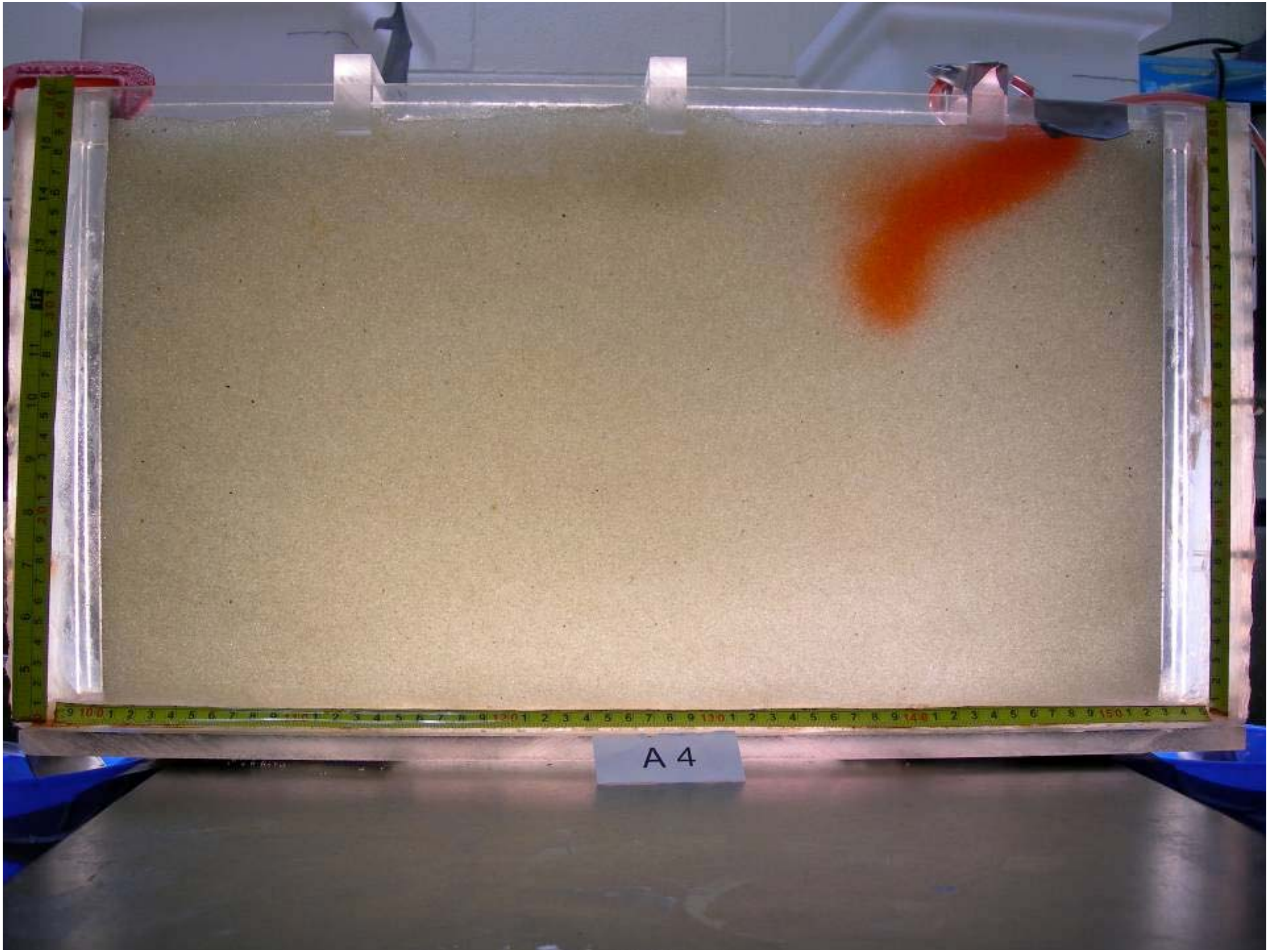
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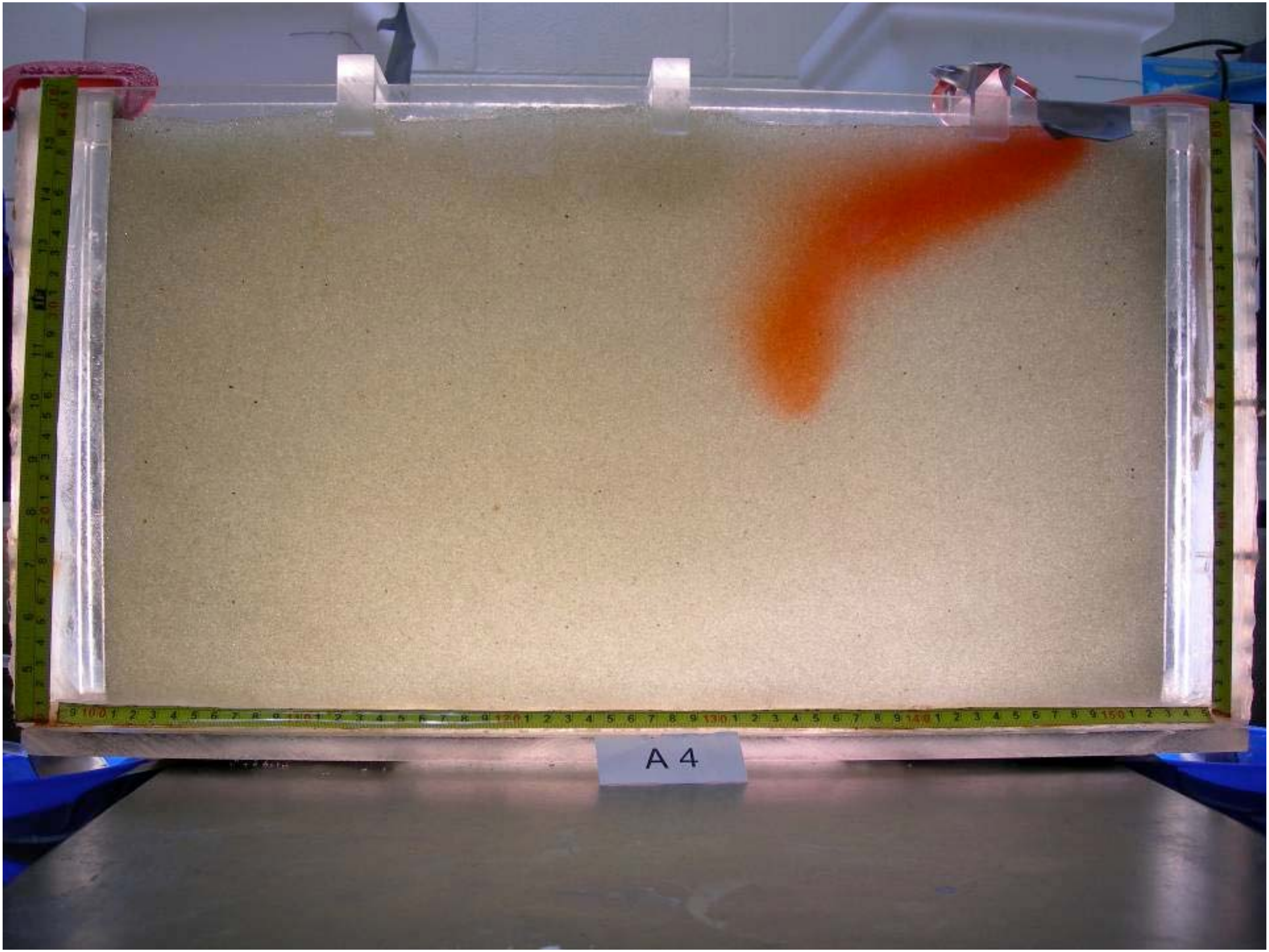
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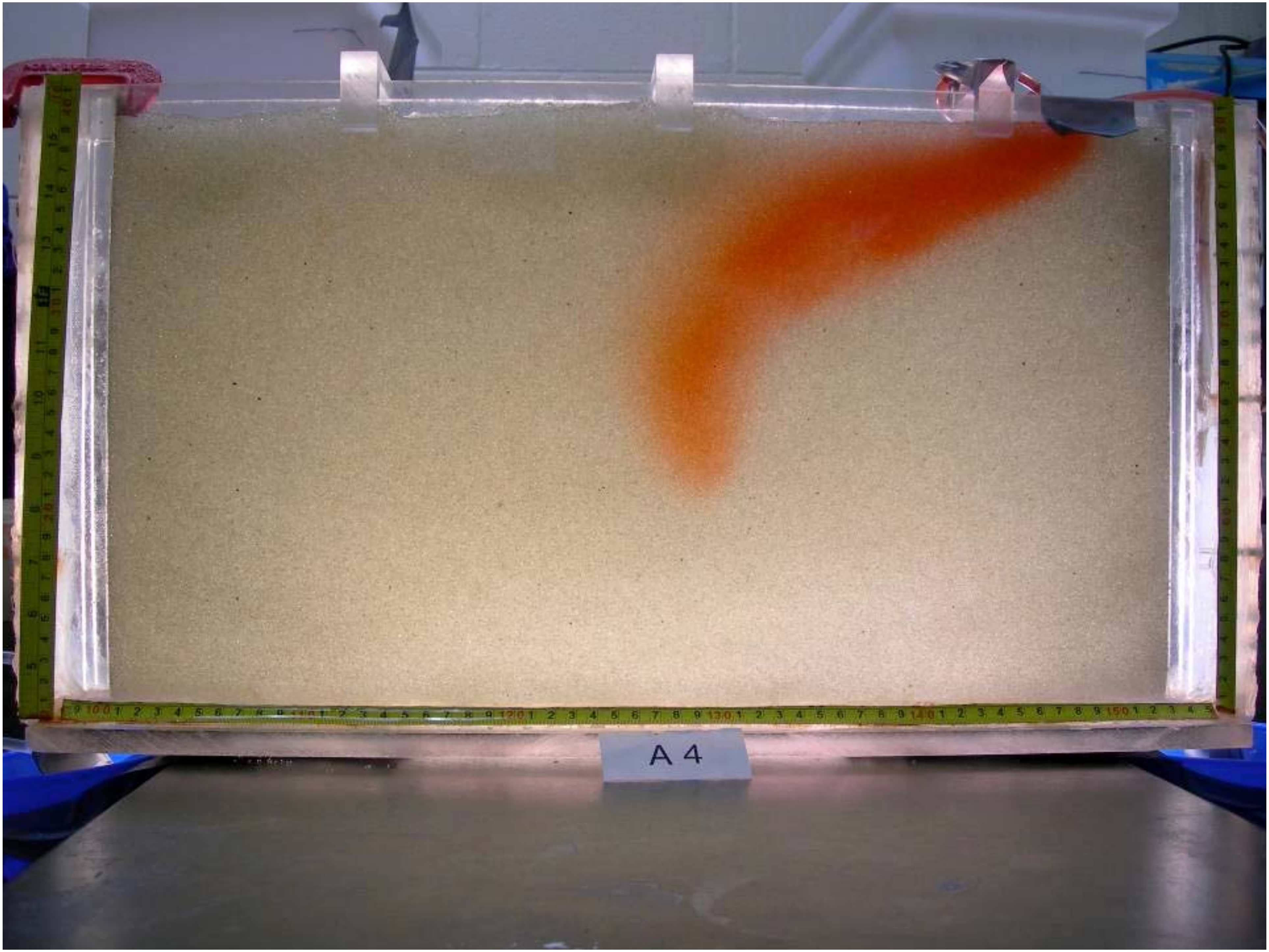
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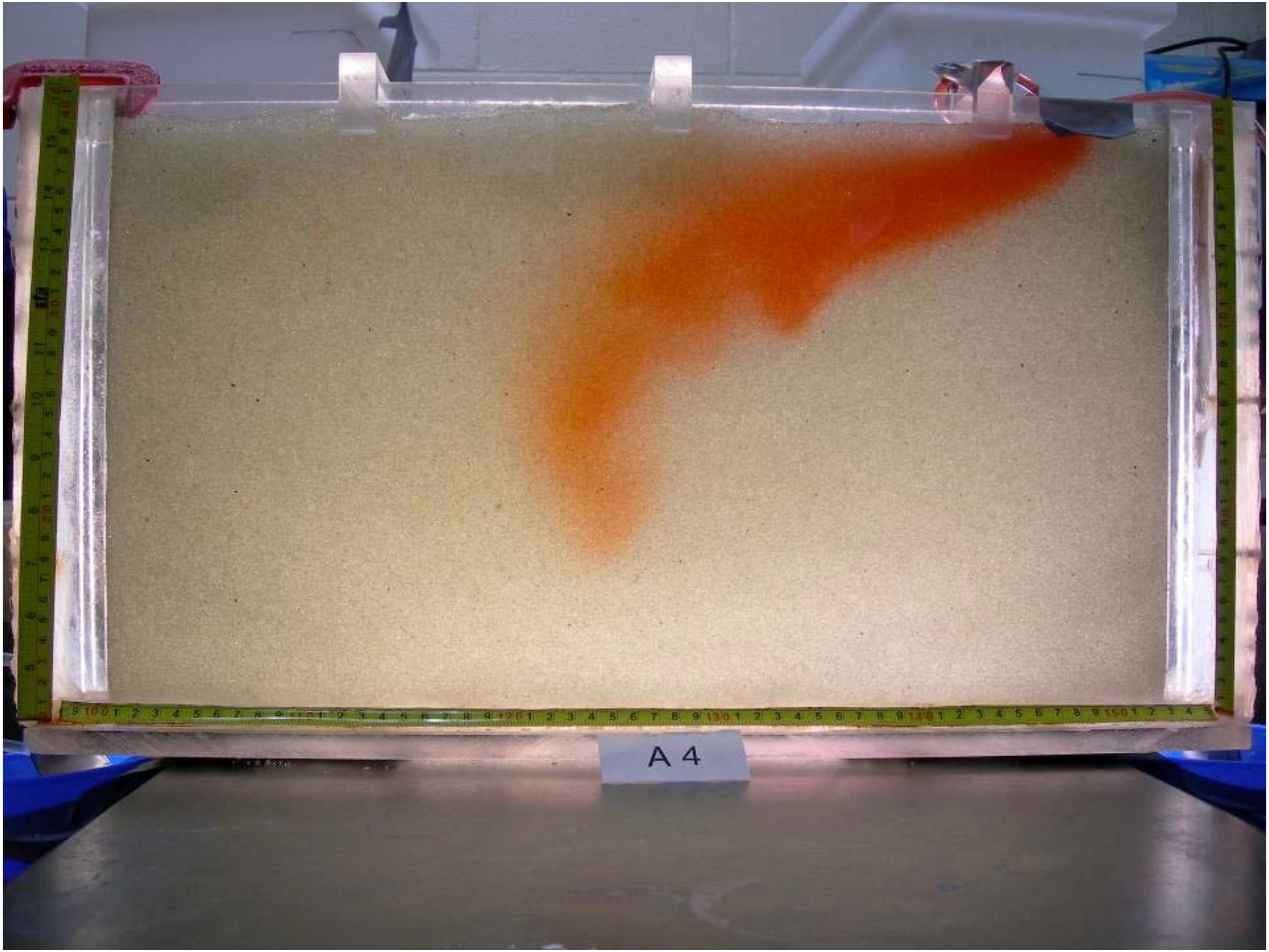
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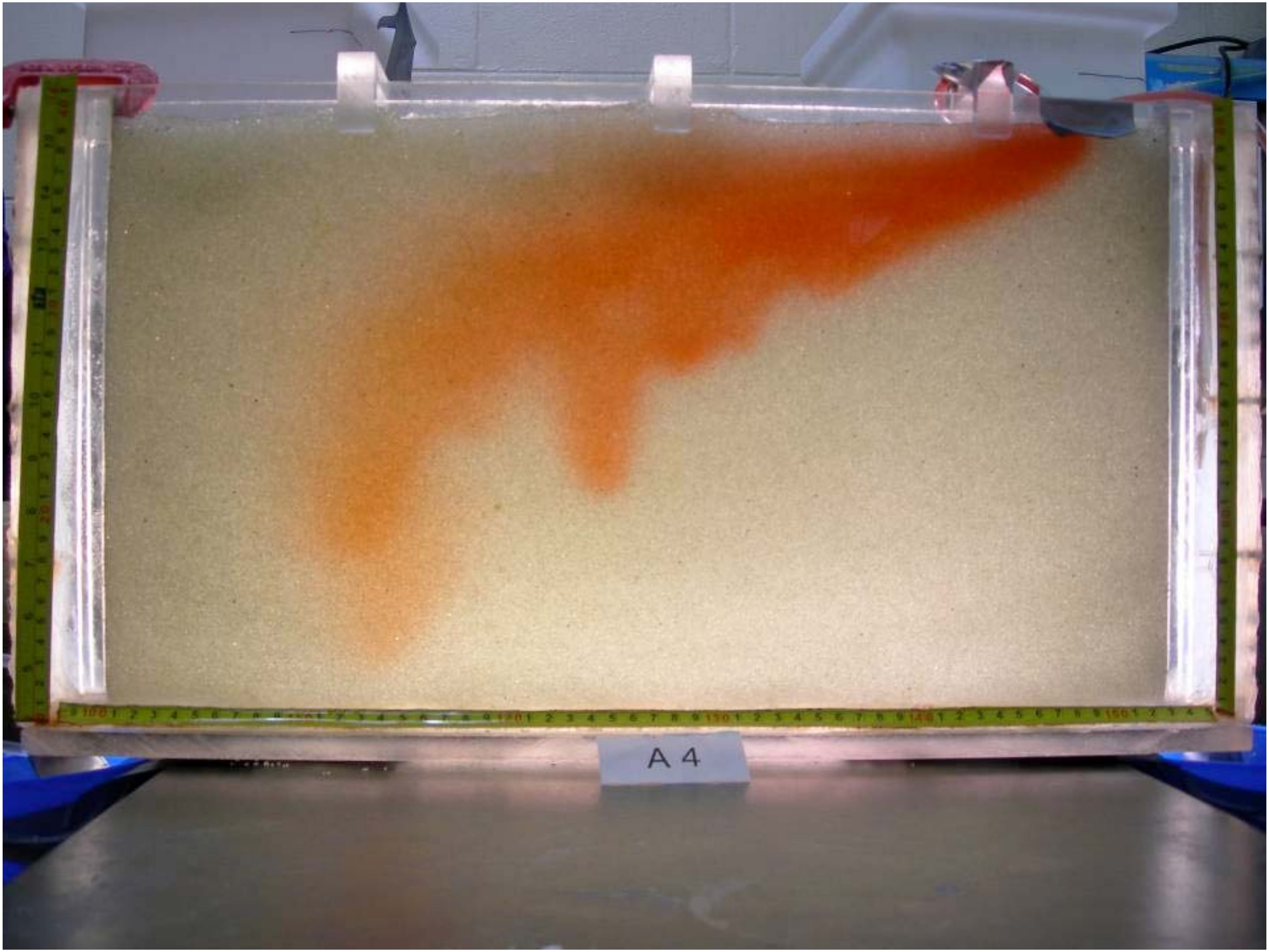
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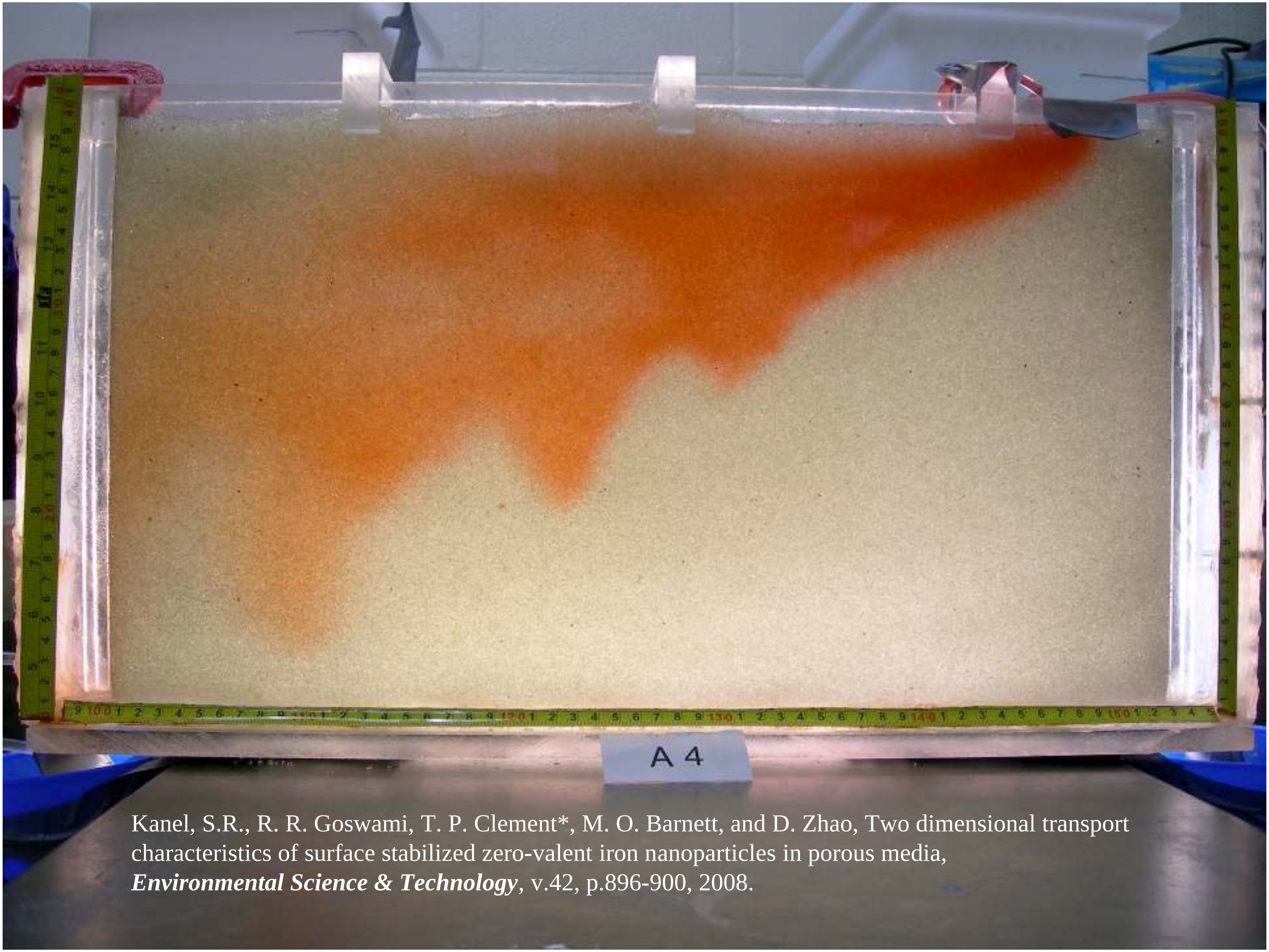
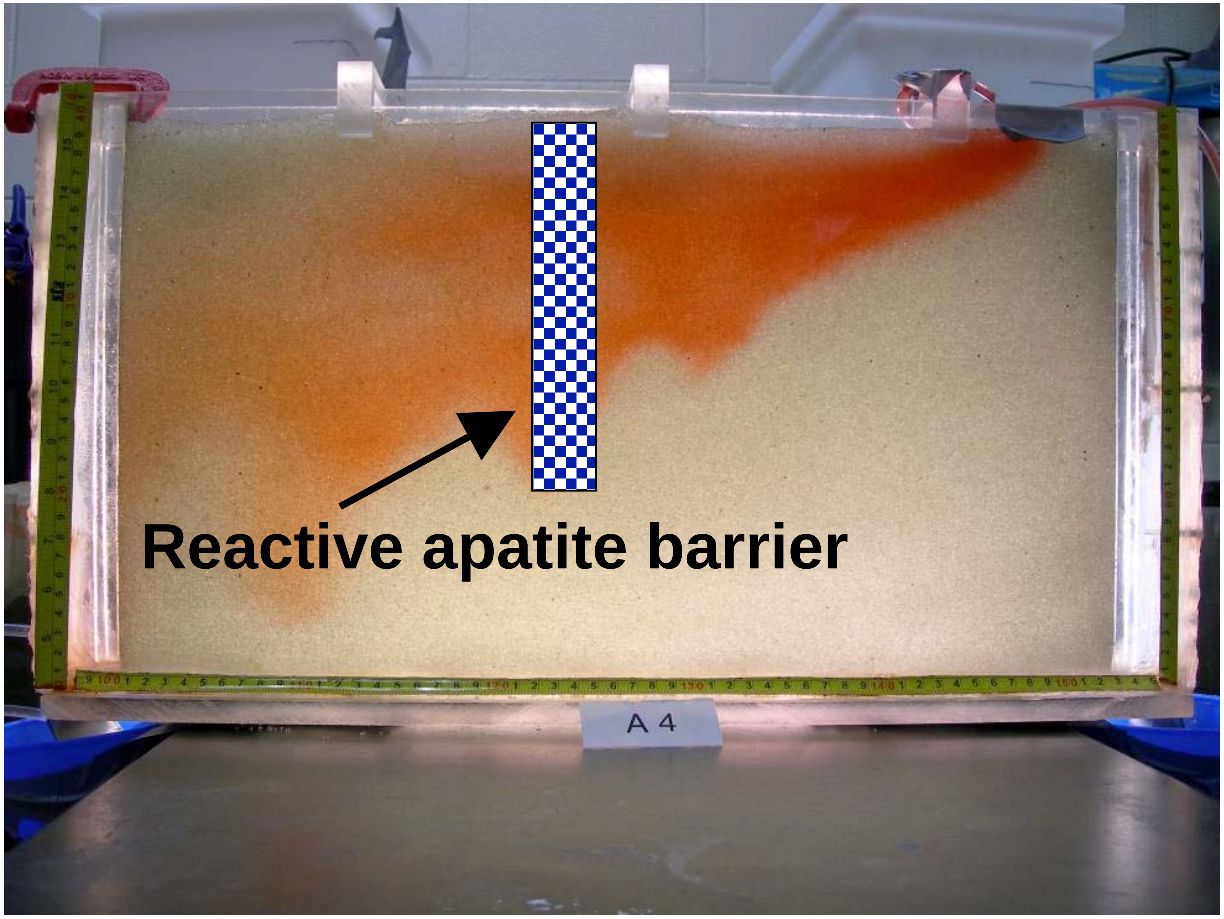


Kanel, S.R., R. R. Goswami, T. P. Clement*, M. O. Barnett, and D. Zhao, Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media, ***Environmental Science & Technology***, v.42, p.896-900, 2008.

Future work



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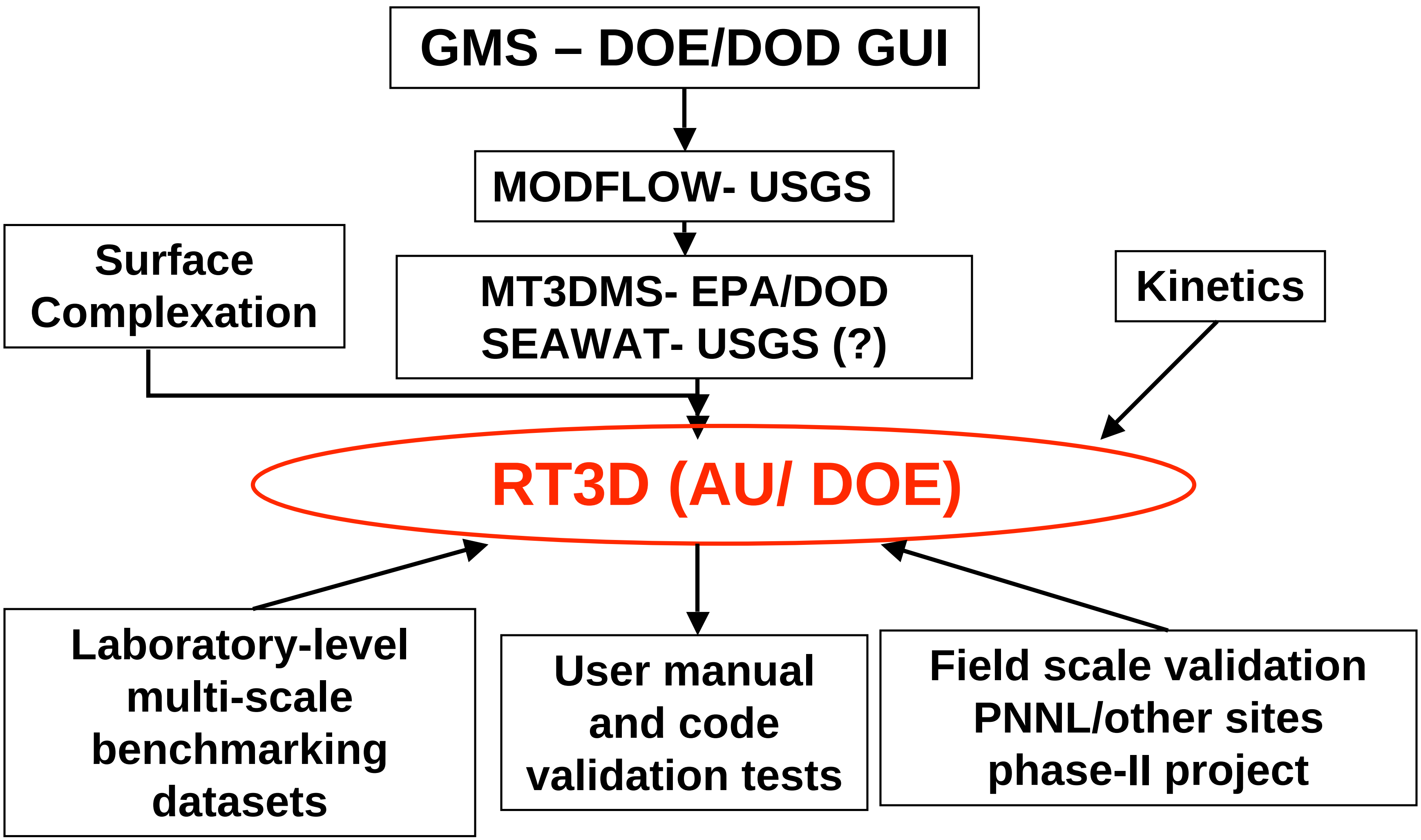
Development of a MODFLOW-based Reactive Transport Modeling System



RT3D- Governing equations

Aqueous phase reactive transport equations

[illegible]

Solid (soil) phase reaction equations

[illegible]

- C is aqueous-phase solute concentration (mobile component)
- r is the specie reaction terms (either kinetics or equilibrium)

(tilde symbol is used to represent solid-phase concentrations (immobile component)

Progress related to RT3D work

- Integrated a surface complexation modeling package within RT3D (AU)
- Developed methods to run RT3D in shared memory, multi-processor systems (BYU)
- Updated RT3D to MT3DMS standard (2006 version)
- GMS interface (BYU)
- Derived a new set of analytical solutions for solving radioactive chemical transport equations (AU)

New Analytical Solution for 1-D transport with radio-active decay

$$R_i \frac{\partial c_i(x,t)}{\partial t} + v\frac{\partial c_i(x,t)}{\partial x} - D_x \frac{\partial^2 c_i(x,t)}{\partial x^2} = y_i k_{i-1} c_{i-1}(x,t) - k_i c_i(x,t)\ ;\ \forall\, i = 2, 3, \ldots n$$

$$= -k_i c_i(x,t)\ ;\ i = 1$$

$$;\ \forall\, t > 0\ \ and\ \ 0 < x < \infty$$

$$c_i(x,t) = \sum_{i_1=1}^{i}\left[\left(\prod_{i_2=i_1+1}^{i} y_{i_2} k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\sum_{i_3=1}^{i_1}\left\{G_1^1 + h\left(G_1^1\right) G_2^1\right\}\right] + \sum_{i_1=1}^{i}\left[R_{i_1} c_{i_1}^{o}\left(\prod_{i_2=i_1+1}^{i} y_{i_2} k_{i_2-1}\right)\sum_{i_2=i_1}^{i}\left\{G_1^2 + h\left(G_1^2\right) G_2^2\right\}\right]\ ;\ \forall\, i = 1, 2, \ldots n$$

$$G_1^1 = \sum_{i_4=i_1,\left(i_4\neq i_2, i_4\neq i^*\right)}^{i} \frac{B_{i_1}^{i_3}\left\langle \begin{array}{l} F_{i_2,i_3,0}[x,t] - u(t-t_o)e^{\left(-\lambda_{i_3} t_o\right)}F_{i_2,i_3,0}[x,(t-t_o)] \\ -F_{i_2,i_2,i_4}[x,t] + u(t-t_o)e^{\left(-\lambda_{i_3} t_o\right)}F_{i_2,i_2,i_4}[x,(t-t_o)] \end{array}\right\rangle}{\left(a_{i_2,i_4} - \lambda_{i_3}\right)\left(\prod_{i_5=i^*} -k_{i_2,i_5}\right)\left(-R_{i_2,i_4}\right)\prod_{i_5=i_1,\left(i_5\neq i_2, i_5\neq i_4, i_5\neq i^*\right)}^{i} -R_{i_2,i_5}\left(a_{i_2,i_5} - a_{i_2,i_4}\right)}$$

$$G_2^1 = \frac{B_{i_1}^{i_3}\left\langle F_{i_2,i_3,0}[x,t] - u(t-t_o)e^{\left(-\lambda_{i_3} t_o\right)}F_{i_2,i_3,0}[x,(t-t_o)]\right\rangle}{\prod_{i_4=i^*} -k_{i_2,i_4}}$$

$$G_1^2 = \sum_{i_3=i_1,\left(i_3\neq i_2, i_3\neq i^*\right)}^{i} \frac{\left\langle F_{i_2,i_1,-i_2}[x,t] - e^{\left(-\mu_{i_1}x - a_{i_1,-i_2}t\right)} - F_{i_2,i_2,i_3}[x,t] + e^{\left(-\mu_{i_1}x - a_{i_2,i_3}t\right)}\right\rangle}{\left(a_{i_2,i_3} - a_{i_1,-i_2}\right)R_{i_2}\left(\prod_{i_4=i^*} -k_{i_2,i_4}\right)R_{i_2,i_3}\prod_{i_4=i_1,\left(i_4\neq i_2, i_4\neq i_3, i_4\neq i^*\right)}^{i} -R_{i_2,i_4}\left(a_{i_2,i_4} - a_{i_2,i_3}\right)}$$

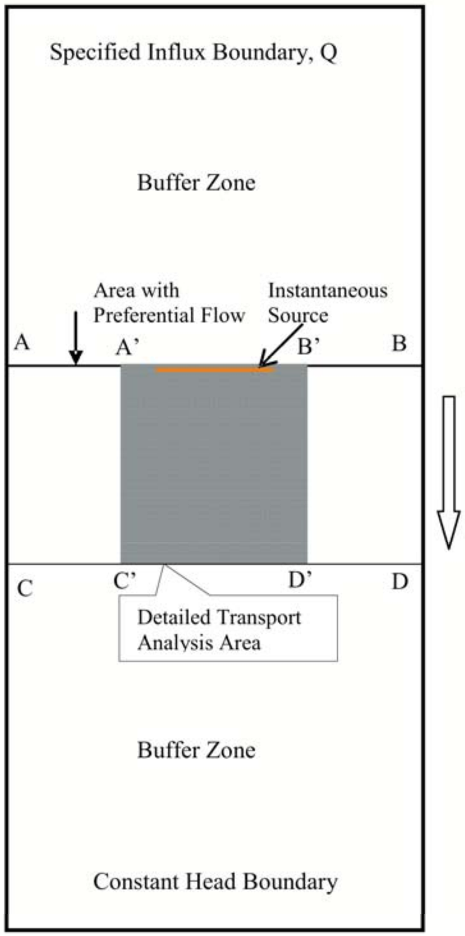
$$G_2^2 = \frac{-\left\langle F_{i_2,i_1,-i_2}[x,t] - e^{\left(-\mu_{i_1}x - a_{i_1,-i_2}t\right)}\right\rangle}{R_{i_2}\prod_{i_3=i^*} -k_{i_2,i_3}}$$

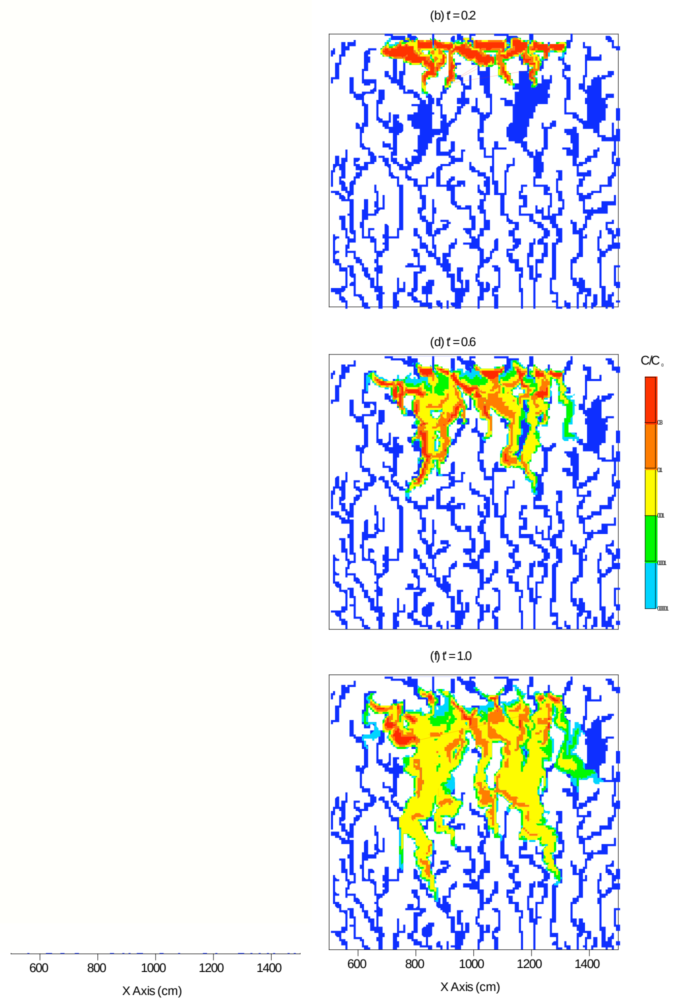
1) Srinivasan, V. and T.P. Clement, Analytical solutions for sequentially coupled one-dimensional reactive transport – Part I: Mathematical Derivations, ***Advances in Water Resources***, v. 31(2), P. 203-218, 2008.
2) Srinivasan, V. and T.P. Clement, Analytical solutions to reactive flows Part II: Implementation and Testing, ***Advances in Water Resources***, v. 31(2), P. 219-232, 2008

Scaling chemically heterogeneous channel networks in RT3D simulations

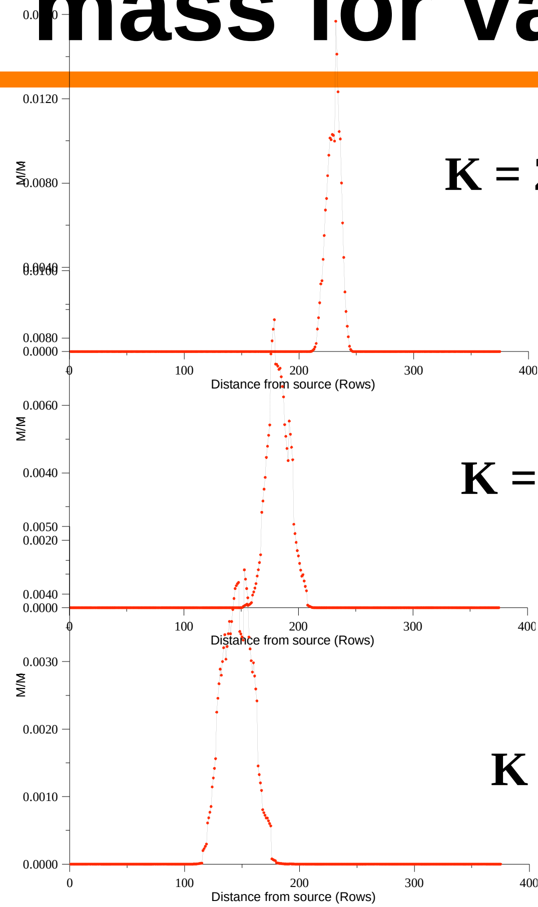
- Natural systems contain small scale heterogeneities embedded within larger scales
- Research question: Can we upscale a system involving a network of small scale chemical heterogeneities?
- What will be an equivalent “dual-domain type” up-scaled model for this system?
- We are currently exploring hydraulically homogeneous (same K) but chemically heterogeneous systems (channel and matrix Kd values are different)

Can we upscale this system? Move from decimeter grids to realistic field-scale grids?





Integrated mass for various Rc & Rm



K = 2.20 m/day; Rm=1.1, Rc=1.0

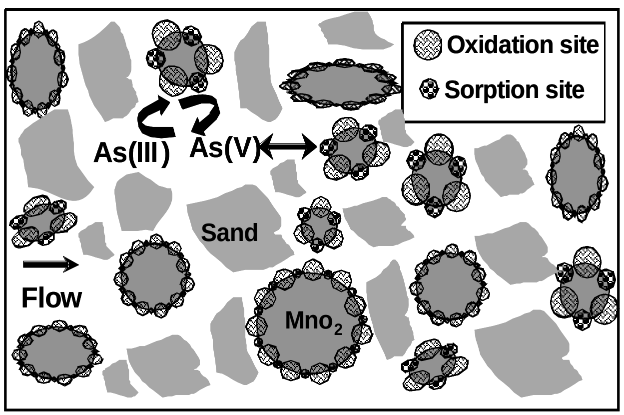
K = 2.20 m/day; Rm=1.5, Rc=1.0

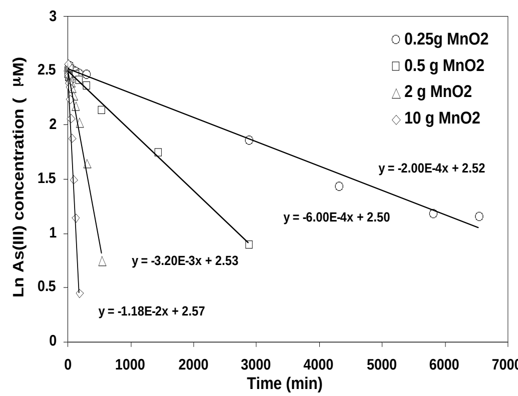
K = 2.20 m/day; Rm=2.0, Rc=1.0

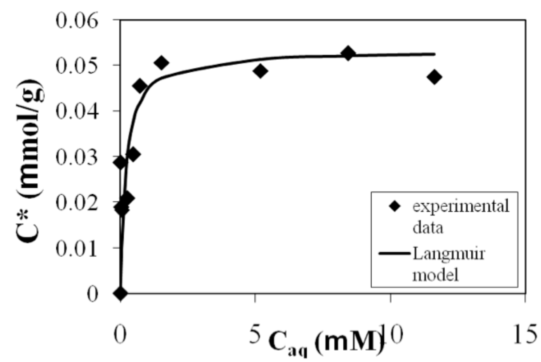
This systems appears to be Gaussian, should be directly scalable. How about systems with non-linear isotherms coupled to hydraulic heterogeneities?

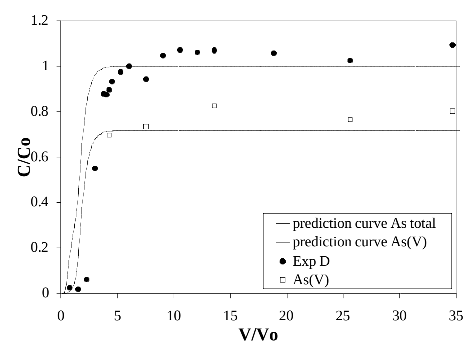
Scaling As sorption and reactive transport with MnO_2 minerals (pyrolusite)

- Completed batch studies to quantify oxidation kinetics and sorption of As(III)/As(V) and MnO_2 interaction
- Scaled kinetic models to predict column-scale transport









Radu, T., Kumar, A., T.P. Clement, G. Jeppu, M.O. Barnett, Development of a scalable model for predicting arsenic transport coupled with oxidation and adsorption reactions, ***Journal of Contaminant Hydrology***, v.95, pages 30–41, 2008.

Research Publications

2D reactive iron transport work

1) Kanel, S.R., R. R. Goswami, T. P. Clement et al., Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media, ES&T, v.42, p. 896-900, 2008.

Analytical solution work

2) Srinivasan, V. and T.P. Clement, Analytical solutions for sequentially coupled 1-D reactive transport problems – Part I: Mathematical Derivations, Adv. in Water Resour., v. 31(2), p. 203-218, 2008.

3) Srinivasan, V. and T.P. Clement, Analytical solu.– Part II: Special Cases and Testing, Adv. in Water Resour., v. 31(2), p. 219-232, 2008.

4) Srinivasan, V., T.P. Clement, and K.K. Lee, Domenico model – Is it valid? Ground Water, v45 (2), p. 136-146, 2007.

MnO_2 sorption and kinetics scaling work

5) Radu, T., A. Kumar, T.P. Clement et al., Development of a scalable model for predicting arsenic transport coupled with oxidation and adsorption reactions, J. of Cont. Hydrology, v.95, p. 30–41, **2008.**

Surface complexation models for Uranium sorption

6) Phillippi, J.M., V.A. Loganathan, et al., M.J. McIndoe et al., Theoretical solid/solution ratio effects on adsorption and transport: U(VI) and Carbonate, Soil Sci. Soc. Am. J, v.71, p.329-335, 2007.

7) Romero-Gonzalez, M.R., T. Cheng, M.O. Barnett et al., Surface complexation modeling of the effects of phosphate on U(VI) adsorption, Radiochimica Acta, v.95(5),p. 251-259, 2007.

Submitted

8) Goswami, R., B. Ambale, T.P. Clement, Error Estimation of Concentrations Measurements obtained from Image Analysis, submitted to Vadose Zone Journal, 2008.

Future work

Draft Manuscripts Under Preparation

1) Loganathan et al: Scaling of U(VI) adsorption onto synthetic iron oxide-coated sands.
2) Jeppu et al: Scaling Arsenate Adsorption on goethite coated sand: Laboratory Experiments and Surface Complexation Modeling.
3) Kanel et al: Removal of uranium using various forms of synthetic and natural hydroxyapatites.
4) Cao et al: Scaling variable sorption porous media containing high or low retardation reactive channels.
5) McLaughlin et al: A shared-memory parallel programming paradigm for solving reactive transport.

Acknowledgements

- Co-PIs
  - Prof. Mark Barnett (and his environmental geochemistry team at Auburn University)
  - Prof. Chunmiao Zheng (and his MT3DMS development team at the University of Alabama)
  - Prof. Norman Jones (and his GMS development team at Brigham Young University)

Collaborators

- CSIRO-Australia and EU Corona Project
  - Dr. Henning Prommer (collaborator)
  - Dr. Massimo Rolle, Univ. of Turin, Italy (collaborator)
- University of Wisconsin- Madison
  - Dr. Eric Roden (collaborator)
- Pacific Northwest National Laboratory
  - Christian Johnson (collaborator)
  - Michel Truex (collaborator)

Students/post-docs

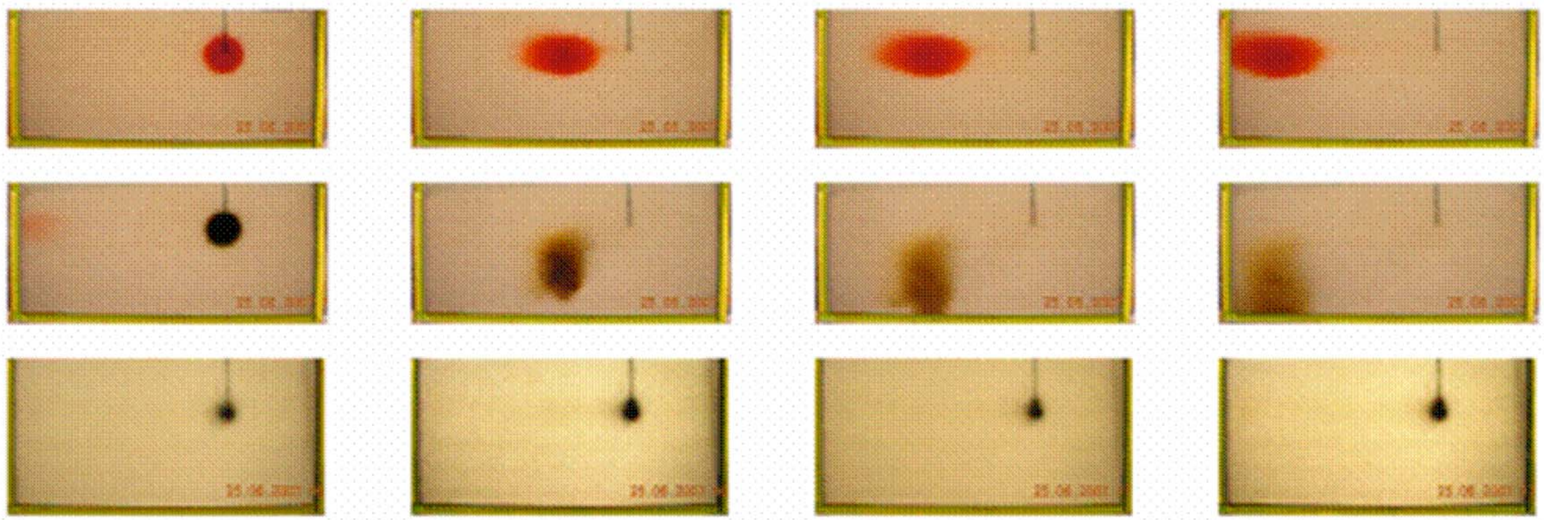
- 1 post-doc Dr Kanel (AU)
- 1 Fulbright Fellow (Dr. Elena Abarca, Spain)
- 6 PhD students (Radu, Goswami, Jeppu, Loganathan, Rolle, Cao)
- 9 Masters students (Kumar, Hartzog, Brakefield, Kuo, Hogan, Shresta, Ayalur, Srinivasan, McLaughlin)
- Several under-graduate students

Question?

- **Web pages**
  - http://www.eng.auburn.edu/users/clemept/
  - RT3D: http://bioprocess.pnl.gov/rt3d.htm

Two-dimensional physical models

(a)
(b)
(c)

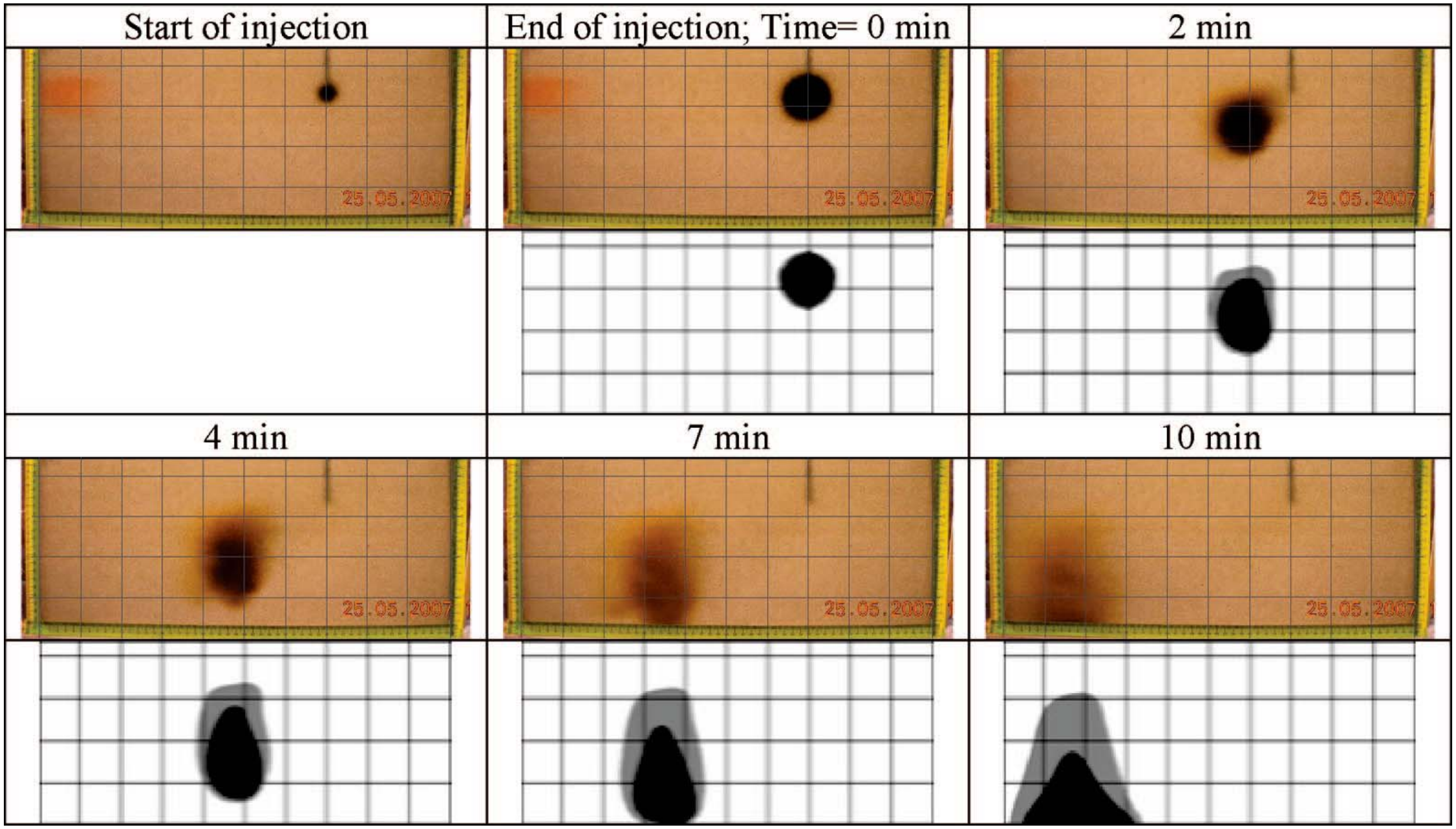


Density driven transport of reactive iron nano-particles

a) Tracer b) stablized INP c) unstablized INP

Kanel, S.R., R. R. Goswami, T. P. Clement*, M. O. Barnett, and D. Zhao, Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media, ***Environmental Science & Technology***, v.42, p.896-900, 2008.

Lab data and model predictions for density-driven INP transport



Kanel, S.R., R. R. Goswami, T. P. Clement*, M. O. Barnett, and D. Zhao, Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media, ***Environmental Science & Technology***, v.42, p.896-900, 2008.